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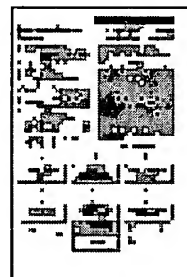
Abstract: **PROBLEM TO BE SOLVED:** To provide a new technique for synthesizing a functional silicon material such as silicon nanotubes, silicon fullerenes, hollow onion-like silicon, hollow onion-like silicon containing a metal or the like in a high yield and in a high purity.

**SOLUTION:** This method for producing a functional silicon material comprising at least one kind of silicon nanotubes, silicon fullerenes, hollow onion-like silicon and hollow onion-like silicon containing a metal comprises irradiating and reacting a polysilane material containing at least one kind of Si=Si bonds and Si≡Si bonds with at least one of light, electron beams and ion beams, heating and reacting the polysilane material containing at least one kind of Si=Si bonds and Si≡Si bonds, or subjecting the polysilane material containing at least one kind of Si=Si bonds and Si≡Si bonds to an irradiation treatment and a heating treatment to react the material.

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Family: **None**
 Forward References: **Go to Result Set: Forward references (1)**

PDF	Patent	Pub.Date	Inventor	Assignee	Title
<input checked="" type="checkbox"/>	<a href="#">DE10345157A1</a>	2005-05-19	DUESBERG, GEORG	Infineon Technologies AG	<a href="#">Wärmeleitende Verpackung von elektronischen Schaltungseinheiten</a>

 Other Abstract [CHEMABS 132\(04\)037405F](#) [CHEMABS 132\(04\)037405F](#) [DERABS C2000-174181](#) [DERABS C2000-174181](#)


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(54)【発明の名称】 機能性珪素材料の製法

(57)【要約】

【課題】高収率かつ高純度で珪素ナノチューブ、珪素フラレン、中空オニオンライク珪素、金属を内包する中空オニオンライク珪素などの機能性珪素材料を合成する新規な技術を提供することを主な目的とする。

【解決手段】-Si=Si-および-Si≡Si-の少なくとも1種を含むポリシラン材料に対し光、電子線およびイオンビームの少なくとも1種を照射することにより、或いは-Si=Si-および-Si≡Si-の少なくとも1種を含むポリシラン材料を加熱することにより、或いは-Si=Si-および-Si≡Si-の少なくとも1種を含むポリシラン材料を照射処理と加熱処理とに併することにより、反応させて、珪素ナノチューブ、珪素フラレン、中空オニオンライク珪素および金属を内包する中空オニオンライク珪素の少なくとも1種を形成させることを特徴とする機能性珪素材料の製法。

## 【特許請求の範囲】

【請求項1】 $-Si=Si-$ および $-Si\equiv Si-$ の少なくとも1種を含むポリシラン材料に対し光、電子線およびイオンビームの少なくとも1種を照射することにより、或いは $-Si=Si-$ および $-Si\equiv Si-$ の少なくとも1種を含むポリシラン材料を加熱することにより、或いは $-Si=Si-$ および $-Si\equiv Si-$ の少なくとも1種を含むポリシラン材料を照射処理と加熱処理とに供することにより、反応させて、珪素ナノチューブ、珪素フラレン、中空オニオンライク珪素および金属を内包する中空オニオンライク珪素の少なくとも1種を形成させることを特徴とする機能性珪素材料の製法。

【請求項2】照射光として、波長300～1200nm、出力0.1～10mJ/cm<sup>2</sup>のレーザー光を用いる請求項1に記載の機能性珪素材料の製法。

【請求項3】照射光として、波長400～800nm、出力0.5～5mJ/cm<sup>2</sup>のレーザー光を用いる請求項2に記載の機能性珪素材料の製法。

【請求項4】電子線照射を $10^{-2}$ ～ $10^{-7}$ torrの減圧下に、加速電圧1～2000KVで行う請求項1に記載の機能性珪素材料の製法。

【請求項5】電子線照射を $10^{-3}$ ～ $10^{-5}$ torrの減圧下に、加速電圧1～2000KVで行う請求項4に記載の機能性珪素材料の製法。

【請求項6】電子線照射を $10^{-2}$ ～ $10^{-7}$ torrの減圧下に、加速電圧50～1000KVで行う請求項4に記載の機能性珪素材料の製法。

【請求項7】電子線照射を $10^{-3}$ ～ $10^{-5}$ torrの減圧下に、加速電圧50～1000KVで行う請求項6に記載の機能性珪素材料の製法。

【請求項8】イオンビーム照射を $10^0$ ～ $10^{-4}$ torrの減圧下に電離させたHeイオン或いはArイオンを用いて、加速電圧100V～10kVおよびイオン電流0.01～100mA/cm<sup>2</sup>の条件下に行う請求項1に記載の機能性珪素材料の製法。

【請求項9】イオンビーム照射を $10^{-1}$ ～ $10^{-8}$ torrの減圧下に電離させたHeイオン或いはArイオンを用いて、加速電圧100V～10kVおよびイオン電流0.01～100mA/cm<sup>2</sup>の条件下に行う請求項8に記載の機能性珪素材料の製法。

【請求項10】イオンビーム照射を $10^0$ ～ $10^{-4}$ torrの減圧下に電離させたHeイオン或いはArイオンを用いて、加速電圧200V～1kVおよびイオン電流0.1～10mA/cm<sup>2</sup>の条件下に行う請求項8に記載の機能性珪素材料の製法。

【請求項11】イオンビーム照射を $10^{-1}$ ～ $10^{-8}$ torrの減圧下に電離させたHeイオン或いはArイオンを用いて、加速電圧100V～10kVおよびイオン電流0.01～100mA/cm<sup>2</sup>の条件下に行う請求項8に記載の機能性珪素材料の製法。

【請求項12】加熱を圧力760～ $10^{-6}$ torrおよび温度100～2000℃の条件下に行う請求項1に記載の機能性珪素材料の製法。

【請求項13】加熱を圧力 $10^{-1}$ ～ $10^{-3}$ torrおよび200～1

500℃の条件下に行う請求項12に記載の機能性珪素材料の製法。

【請求項14】加熱を圧力760～ $10^{-4}$ torrのHeまたはAr雰囲気中温度100～2000℃の条件下に行う請求項12に記載の機能性珪素材料の製法。

【請求項15】加熱を圧力760～ $10^{-4}$ torrのHeまたはAr雰囲気中温度200～1500℃の条件下に行う請求項14に記載の機能性珪素材料の製法。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】本発明は、珪素ナノチューブ、珪素フラレン、中空オニオンライク珪素および金属を内包する中空オニオンライク珪素の少なくとも1種を含む機能性珪素材料の製法に関する。

【0002】なお、本発明において、「中空オニオンライク珪素」とは、中心部が中空であって、その周囲にオニオン様に珪素積層構造が発達している球状或いは多面体状の珪素粒子を意味する。この様な中空オニオンライク珪素においては、珪素積層は、単層から数十層に積層している。

【0003】また、「金属を内包する中空オニオンライク珪素」とは、上記の「中空オニオンライク珪素」の中心部の中空内に金属粒子が存在する球状或いは多面体状の珪素粒子を意味する。内包する金属は、特に限定されないが、例えば、Mg、Al、Auなどが挙げられる。

## 【0004】

【従来の技術】従来、ナノサイズの高機能炭素材（カーボンナノチューブ（以下に単に「ナノチューブ」ということがある）、フラレン、中空オニオンライクカーボン、金属を内包する中空オニオンライクカーボンなど）は、非晶炭素、グラファイトなどの炭素材料を原料として、カーボンアーク法、スパッタ法、レーザー光照射法などにより、気相で合成されている。

【0005】一方、珪素材料に関しては、気相での珪素クラスター合成の研究例はあるが、機能性炭素材料の炭素を珪素と置き換えた珪素ナノチューブ、珪素フラレン、中空オニオンライク珪素、金属を内包する中空オニオンライク珪素などを合成した例はない。すなわち、上記の物理的な方法によれば、高温による原料の分解、蒸発、再結合、堆積などにより、機能性炭素材料は形成されるが、この方法を珪素系材料の合成に適用する場合には、原料の分解、蒸発が起こりにくいといった問題点がある。

【0006】機能性珪素材料は、種々の優れた特性を備えているので、実用的な合成技術が確立されるならば、耐環境材料、耐熱性材料、耐摩耗性材料、水素吸蔵材料、電子線放射エミッター、その他の電子材料などの広い分野での応用が期待されている。さらに、機能性珪素材料を基板上に配列した高純度薄膜を形成し得る技術が確立された場合には、その有用性もさらに高まるものと

予測される。

【0007】

【発明が解決しようとする課題】従って、本発明は、高収率かつ高純度で珪素ナノチューブ、珪素フラレン、中空オニオンライク珪素、金属を内包する中空オニオンライク珪素などの機能性珪素材料を合成する新規な技術を提供することを主な目的とする。

【0008】

【課題を解決するための手段】本発明者は、上記の様な技術の現状に鑑みて、研究を進めた結果、反応性の二重結合および三重結合の少なくとも一方を有するポリシラン材料を原料として、珪素ナノチューブなどの機能性珪素材料を合成する新たな技術を完成すべく、鋭意研究を重ねた結果、電気化学還元的手法を用いることにより、常温付近で反応性の二重結合および／または三重結合を有するポリシラン材料（プリカーサー）を合成し、このプリカーサーに比較的低温で光、電子線、イオンビームなどを照射するか或いはこのプリカーサーを加熱処理することにより、架橋反応させて、機能性珪素材料を製造することに成功した。

【0009】すなわち、本発明は、下記に示す機能性珪素材料の新しい製造方法を提供するものである；

1.  $\text{-Si=Si-}$ および $\text{-Si}\equiv\text{Si-}$ の少なくとも1種を含むポリシラン材料に対し光、電子線およびイオンビームの少なくとも1種を照射することにより、或いは $\text{-Si=Si-}$ および $\text{-Si}\equiv\text{Si-}$ の少なくとも1種を含むポリシラン材料を加熱することにより、或いは $\text{-Si=Si-}$ および $\text{-Si}\equiv\text{Si-}$ の少なくとも1種を含むポリシラン材料を照射処理と加熱処理とに供することにより、反応させて、珪素ナノチューブ、珪素フラレン、中空オニオンライク珪素および金属を内包する中空オニオンライク珪素の少なくとも1種を形成させることを特徴とする機能性珪素材料の製法。

【0010】2. 照射光として、波長300～1200nm、出力0.1～10mJ/cm<sup>2</sup>のレーザー光を用いる上記項1に記載の機能性珪素材料の製法。

【0011】3. 照射光として、波長400～800nm、出力0.5～5mJ/cm<sup>2</sup>のレーザー光を用いる上記項2に記載の機能性珪素材料の製法。

【0012】4. 電子線照射を $10^{-2}$ ～ $10^{-7}$ torrの減圧下に、加速電圧1～2000KVで行う上記項1に記載の機能性珪素材料の製法。

【0013】5. 電子線照射を $10^{-3}$ ～ $10^{-5}$ torrの減圧下に、加速電圧1～2000KVで行う上記項4に記載の機能性珪素材料の製法。

【0014】6. 電子線照射を $10^{-2}$ ～ $10^{-7}$ torrの減圧下に、加速電圧50～1000KVで行う上記項4に記載の機能性珪素材料の製法。

【0015】7. 電子線照射を $10^{-3}$ ～ $10^{-5}$ torrの減圧下に、加速電圧50～1000KVで行う上記項6に記載の機能性珪素材料の製法。

【0016】8. イオンビーム照射を $10^{-2}$ ～ $10^{-4}$ torrの減圧下に電離させたHeイオン或いはArイオンを用いて、加速電圧100V～10kVおよびイオン電流0.01～100mA/cm<sup>2</sup>の条件下に行う上記項1に記載の機能性珪素材料の製法。

【0017】9. イオンビーム照射を $10^{-1}$ ～ $10^{-3}$ torrの減圧下に電離させたHeイオン或いはArイオンを用いて、加速電圧100V～10kVおよびイオン電流0.01～100mA/cm<sup>2</sup>の条件下に行う上記項8に記載の機能性珪素材料の製法。

【0018】10. イオンビーム照射を $10^{-2}$ ～ $10^{-4}$ torrの減圧下に電離させたHeイオン或いはArイオンを用いて、加速電圧200V～1kVおよびイオン電流0.1～10mA/cm<sup>2</sup>の条件下に行う上記項8に記載の機能性珪素材料の製法。

【0019】11. イオンビーム照射を $10^{-1}$ ～ $10^{-3}$ torrの減圧下に電離させたHeイオン或いはArイオンを用いて、加速電圧100V～10kVおよびイオン電流0.01～100mA/cm<sup>2</sup>の条件下に行う上記項8に記載の機能性珪素材料の製法。

【0020】12. 加熱を圧力760～ $10^{-6}$ torrおよび温度100～2000℃の条件下に行う上記項1に記載の機能性珪素材料の製法。

【0021】13. 加熱を圧力 $10^{-1}$ ～ $10^{-3}$ torrおよび200～1500℃の条件下に行う上記項12に記載の機能性珪素材料の製法。

【0022】14. 加熱を圧力760～ $10^{-4}$ torrのHeまたはAr雰囲気中温度100～2000℃の条件下に行う上記項12に記載の機能性珪素材料の製法。

【0023】15. 加熱を圧力760～ $10^{-4}$ torrのHeまたはAr雰囲気中温度200～1500℃の条件下に行う上記項14に記載の機能性珪素材料の製法。

【0024】

【発明の実施の形態】本発明方法は、従来方法と比較して、マイルドな条件下での半化学的合成法であり、化学反応により構造を組み立てて行く新規な機能性珪素材料を製造する技術である。

【0025】本発明方法において原料となる反応性の二重結合および三重結合の少なくとも1種を有するポリシラン材料は、側鎖の全部または一部がハロゲンで置換されているポリシランを、電極還元法により脱ハロゲン化し、二重結合および／または三重結合を有するポリシラン材料を合成する。

【0026】側鎖の全部または一部がハロゲンで置換されているポリシランは、公知の材料であって、例えば、特開昭63-233007号公報などにその製法が詳しく報告されている。従って、その製法は限定されるものではなく、また、置換状態、分子量などの異なる2種以上を混合して使用することもできる。側鎖の一部がハロゲンにより置換されているポリシラン誘導体においては、ハロ

ゲン以外の側鎖基は、水素、メチル、フェニルなどが例示されるが、これらに限定されない。

【0027】また、上記の側鎖がハロゲンで置換されているポリシランから、二重結合および／または三重結合を有するポリシラン材料を合成するには、電極電解還元を行う。電解還元の際には、支持電解質および通電助剤を溶解した非水系溶媒中で、Mg、Al、Znなどの反応性電極を、2電極法においては陽極として、3電極法においては作用電極として用いることが好ましい。

【0028】電解還元の際には、反応性電極(すなわち、2電極法における陽極、或いは3電極法における対電極)としては、マグネシウム、アルミニウムおよび亜鉛の1種またはこれらの合金を使用する。これらの合金としては、特に限定されるものではないが、マグネシア合金(「マグノックス」; Mg=98.89%, Al=1%, Ca=0.1%, Ba=0.01%), アルミニウム合金(「ジュラルミン」; Al=95%, Cu=4.6%, Mg=0.5%), 亜鉛-アルミニウム合金(Zn=78%, Al=22%)などが例示される。

【0029】また、2電極法における陰極および3電極法における作用電極の材料、形状などは、特に限定されない。これらの材料としては、ステンレス鋼、カーボン、白金、金などが例示される。電極形状は、ワイヤー、メッシュ、プレートなどの任意の形状を選択することができる。

【0030】支持電解質としては、LiCl、LiClO<sub>4</sub>、LiBF<sub>4</sub>、NH<sub>4</sub>Cl、NH<sub>4</sub>ClO<sub>4</sub>、NH<sub>4</sub>BF<sub>4</sub>、(CH<sub>3</sub>)<sub>4</sub>NCl、(CH<sub>3</sub>)<sub>4</sub>NClO<sub>4</sub>、(CH<sub>3</sub>)<sub>4</sub>NBF<sub>4</sub>などが挙げられる。これらの中では、LiClがより好ましい。支持電解質の使用割合は、溶媒に対して、通常0.01~10重量%程度であり、より好ましくは0.5~5重量%程度である。

【0031】通電助剤としては、FeCl<sub>2</sub>、Fe(ClO<sub>4</sub>)<sub>2</sub>、Fe(BF<sub>4</sub>)<sub>2</sub>などが挙げられ、これらの中ではFeCl<sub>2</sub>がより好ましい。通電助剤の使用割合は、溶媒に対して、通常0.1~30重量%程度であり、より好ましくは1~20重量%程度である。

【0032】非水系溶媒としては、テトラヒドロフラン、N,N-ジメチルホルムアミド、アセトニトリルなどが挙げられ、これらの中ではテトラヒドロフランがより好ましい。非水系溶媒の使用量は、ハロゲン原子を有する芳香族炭化水素誘導体に対して、通常20~200重量倍程度であり、好ましくは50~100重量倍程度である。

【0033】電解還元反応においては、反応原料であるハロゲン原子を有するポリシラン誘導体に電子が移動し、その反応中間体から脱離する官能基がアニオンとして脱離することにより、ポリシラン誘導体に珪素ラジカルが生成し、隣り合う珪素ラジカルがカップリングする。この反応が連続的に進行することにより、ポリシラン誘導体から、多重結合が高度に発達した珪素材料が得られる。ただし、この電解還元反応においては、隣り合う珪素ラジカルがカップリングするだけでなく、異なる

分子に存在する珪素ラジカルのカップリング(クロスリンク)や、珪素ラジカルの生成点での分解、不均化などの副反応をも伴う。

【0034】そこで、副反応を低減するために、M(dpp e)<sub>2</sub>X<sub>2</sub> [式中、MはFe、CoまたはNi; XはCl、BrまたはI] を触媒として添加し、主反応を優先させる。このM(dpp e)<sub>2</sub>X<sub>2</sub>の使用割合は、溶媒に対して、通常0.01~5重量%程度であり、より好ましくは0.1~2重量%程度である。

【0035】本発明の電極電解還元は、窒素、アルゴンガス、ヘリウムなどの不活性ガス下で行うことが好ましい。

【0036】本発明の電極電解還元の際には、通常5~50V程度の電圧を印加し、より好ましくは10~30V程度の電圧を印加する。

【0037】また、本発明の電極電解還元時の温度は、通常-20~10℃程度の範囲内にあり、より好ましくは-10~5℃程度の範囲内にある。反応時間は、通常5~24時間程度の範囲内にあり、より好ましくは8~12時間程度の範囲内にある。

【0038】本発明方法により得られる珪素材料は、二重結合(-Si=Si-)および三重結合(-Si≡Si-)の少なくとも一方を含む。

【0039】この様な反応性の二重結合および／または三重結合を含むポリシラン材料を原料として、珪素ナノチューブなどの機能性珪素材料を合成する試みは、従来なされていない。

【0040】本発明においては、反応性の二重結合および／または三重結合を含むポリシラン材料をブリーカーとして、これに対し光(例えば、レーザー光)、電子線およびイオンビームの少なくとも1種を照射処理することにより、或いはこの様なポリシラン材料を加熱処理することにより、或いはこの様なポリシラン材料を照射処理および加熱処理することにより、珪素ナノチューブ、珪素フラレン、中空オニオンライク珪素、金属を内包する中空オニオンライク珪素あるいはこれらの2種以上の混在物(以下「目的生成物」ということがある)からなる材料あるいは薄膜を得る。

【0041】目的生成物の合成は、上記の原料ポリシラン材料に対し、レーザー光などの光、電子ビーム、イオンビームなどの少なくとも1種を照射し、或いは原料ポリシラン材料を加熱処理し、或いは原料ポリシラン材料を照射処理および加熱処理(両処理の順序は問わない)して、原料内で反応を生じさせることにより、行うことが出来る。

【0042】原料ポリシラン材料に対し光照射を行う場合には、通常波長300~1200nm程度、出力0.1~10mJ/cm<sup>2</sup>程度、より好ましくは波長400~800nm程度、出力0.5~5mJ/cm<sup>2</sup>程度のレーザー光を使用する。レーザー光の種類は、通常使用されているものが使用でき、特に制限されるものではないが、例えば、Nd:YAGレーザー、Ti:Saレ

ーザー、Dyeレーザー、Dye+SHGレーザー、Ar+レーザー、Kr+レーザーなどが挙げられる。

【0043】原料ポリシラン材料に対し電子線照射を行う場合には、通常 $10^{-2}$ ～ $10^{-7}$  torr程度（より好ましくは $10^{-3}$ ～ $10^{-6}$  torr程度）の減圧下に、加速電圧1～2000kV程度（より好ましくは50～1000kV程度）で照射を行う。

【0044】イオンビーム照射を行う場合には、原料ポリシラン材料を減圧チェンバー（通常 $10^{-2}$ ～ $10^{-4}$  torr程度；より好ましくは $10^{-1}$ ～ $10^{-3}$  torr程度）内に配置し、電離させたHeイオン或いはArイオンを用いて、加速電圧100V～10kV程度（より好ましくは200V～1kV程度）およびイオン電流0.01～100mA/cm<sup>2</sup>程度（より好ましくは0.1～10mA/cm<sup>2</sup>程度）の条件下に照射を行う。

【0045】原料ポリシラン材料に反応エネルギーを付与するために照射を行う場合には、照射源として、レーザー光を使用することがより好ましい。

【0046】原料ポリシラン材料を加熱する場合には、通常760～ $10^{-6}$  torr程度の減圧下（より好ましくは $10^{-1}$ ～ $10^{-3}$  torr程度の圧力下）に100～2000℃程度（より好ましくは、200～1500℃程度）で加熱する。或いは、760～ $10^{-4}$  torr程度のHe或いはAr雰囲気中100～2000℃程度（より好ましくは、200～1500℃程度）でポリシラン材料の加熱を行っても良い。

【0047】さらに、原料ポリシラン材料の処理に際しては、上記の照射処理の少なくとも1種と加熱処理とを併用しても良い。

【0048】

【発明の効果】本発明によれば、以下のような顕著な効果が達成される。

【0049】(1)-Si≡Si-および-Si≡Si-の少なくとも一方を含むポリシラン材料に対し、光、電子ビームおよびイオンビームの少なくとも1種を照射するか、或いはこの様なポリシラン材料を加熱処理するか、或いはこの様なポリシラン材料を照射処理および加熱処理することにより、珪素ナノチューブ、珪素フラレン、中空オニオンライク珪素、金属内包オニオンライク珪素を作製できる。

【0050】(2)ポリシラン材料の処理手段として、光、電子ビームおよびイオンビームによる照射処理ならびに加熱処理を適宜選択することにより、或いは複数の処理を組み合わせることに、珪素ナノチューブ、珪素フラレン、中空オニオンライク珪素および金属内包オニオンライク珪素のいずれかを選択的に作製できる。

【0051】(3)従って、本発明による機能性珪素材料は、耐環境材料、耐熱性材料、耐磨耗性材料、水素吸蔵材料、電子線放射エミッター、その他の電子材料などとして有用である。

【0052】

【実施例】実施例1

機能性珪素材料を以下に示す方法により合成した。

【0053】ポリシラン(HD-(Si(CH<sub>3</sub>)(C<sub>6</sub>H<sub>5</sub>))<sub>n</sub>-OH；n=50)を原料として、ポリシランを塩素化し、塩素化物(HD-(Si(CH<sub>3</sub>)(C<sub>6</sub>H<sub>5</sub>))(Si(CH<sub>3</sub>)(Cl))<sub>n</sub>-OHを形成した後、特開平8-335702号公報に示すポリテトラフルオロエチレンフィルムを反応性陽極で電解還元する方法に準じて、二重結合を有する部分を持つポリシラン材料を合成した。

【0054】すなわち、上記ポリシランの塩素化物を以下の溶媒とともに、フラスコ中に仕込み溶解させた。

【0055】

テトラヒドロフラン	30ml
塩化リチウム	0.8g
塩化第一鉄	0.48g

次いで、フラスコ内をアルゴンガスに置換した後、アルゴンガスでバブリングしながら、フラスコに設置した陽極（マグネシウム）と陰極（ステンレススチール）間に40Vの電圧を印加して、0℃で10時間還元して、二重結合の生成したポリシラン粉末を得、これをテトラヒドロフランで洗浄した後、真空乾燥した。得られた生成物を25%トルエン溶液として、スピンコート法により基板上にポリシラン薄膜を形成させた。

【0056】調製した二重結合を含むポリシラン薄膜をエポキシ樹脂に包埋して、マイクロトームを用いて、透過電子顕微鏡(TEM:HITACHI H7100)による電子線照射処理のためにカットした後、 $10^{-6}$  torrの高真空下、サンプルホルダーを800℃に加熱し、100kVの加速電圧で電子線を照射した。

【0057】その結果、サンプル中に珪素ナノチューブが形成されたことを透過電子顕微鏡で確認できた。

【0058】実施例2

実施例1と同様にして作製した二重結合を含むポリシラン材料サンプルをエポキシ樹脂に包埋して、マイクロトームを用いて、透過電子顕微鏡(TEM:HITACHI H7100)による電子線照射処理のためにカットした後、 $10^{-6}$  torrの高真空下、サンプルホルダーを300℃に加熱し、100kVの加速電圧で電子線を照射した。

【0059】その結果、サンプル中にマグネシウム微粒子を内包するオニオンライク珪素が形成されたことを透過電子顕微鏡で確認できた。このマグネシウム微粒子は、原料を還元する際に、陽極から発生したマグネシウムイオンが金属マグネシウムとして薄膜内に析出したものと考えられる。

【0060】実施例3

実施例2と同様にして作製したマグネシウム微粒子を内包するオニオンライク珪素サンプルを、実施例2の操作に引き続いて、サンプルホルダー温度を800℃に上げて、10分間保持した。その結果、内包されていたマグネシウム粒子が、熔融気化して除去され、サンプル中に中空オニオンライク珪素が形成された。

【0061】実施例4

実施例1と同様にして作製した二重結合を含むポリシラン材料サンプルに対し、減圧チェンバー中( $4 \times 10^{-2}$  torr)でイオンビーム(カウフマン型イオンソース: アルゴンイオンビーム、加速電圧: 500V、イオン電流密度:  $1 \text{ mA/cm}^2$ )を10分間照射した。

【0062】このサンプルをトルエンで抽出し、濃縮した後、HPLCで分離した(カラム: コスモシール Buckyrepバックドカラム)。 $^{13}\text{C}$ -NMRにより、珪素フラレンが形成されていることが確認できた。

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# PATENT ABSTRACTS OF JAPAN

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## **(54) PRODUCTION OF FUNCTIONAL SILICON MATERIAL**

### **(57)Abstract:**

**PROBLEM TO BE SOLVED:** To provide a new technique for synthesizing a functional silicon material such as silicon nanotubes, silicon fullerenes, hollow onion-like silicon, hollow onion-like silicon containing a metal or the like in a high yield and in a high purity.

**SOLUTION:** This method for producing a functional silicon material comprising at least one kind of silicon nanotubes, silicon fullerenes, hollow onion-like silicon and hollow onion-like silicon containing a metal comprises irradiating and reacting a polysilane material containing at least one kind of Si=Si bonds and Si≡Si bonds with at least one of light, electron beams and ion beams, heating and reacting the polysilane material containing at least one kind of Si=Si bonds and Si≡Si bonds, or subjecting the polysilane material containing at least one kind of Si=Si bonds and Si≡Si bonds to an irradiation treatment and a heating treatment to react the material.

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## CLAIMS

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### [Claim(s)]

[Claim 1] - By irradiating at least one sort of light, an electron ray, and an ion beam to the polysilane ingredient containing at least one sort of Si=Si- and -Si\*\*Si- Or by heating the polysilane ingredient containing at least one sort of -Si=Si- and -Si\*\*Si- Or by presenting exposure processing and heat-treatment with the polysilane ingredient containing at least one sort of -Si=Si- and -Si\*\*Si- The process of the functional silicon ingredient characterized by making at least one sort of the hollow-onion-like silicon which is made to react and connotes a silicon nanotube, silicon FURAREN, hollow-onion-like silicon, and a metal form.

[Claim 2] The process of the functional silicon ingredient according to claim 1 using the laser light of the wavelength of 300-1200nm, an output 0.1 - 10 mJ/cm<sup>2</sup> as an exposure light.

[Claim 3] The process of the functional silicon ingredient according to claim 2 using the laser light of the wavelength of 400-800nm, an output 0.5 - 5 mJ/cm<sup>2</sup> as an exposure light.

[Claim 4] The process of the functional silicon ingredient according to claim 1 which performs electron beam irradiation with the acceleration voltage of 1-2000kV to the bottom of reduced pressure of 10<sup>-2</sup> - 10<sup>-7</sup>torr.

[Claim 5] The process of the functional silicon ingredient according to claim 4 which performs electron beam irradiation with the acceleration voltage of 1-2000kV to the bottom of reduced pressure of 10<sup>-3</sup> - 10<sup>-5</sup>torr.

[Claim 6] The process of the functional silicon ingredient according to claim 4 which performs electron beam irradiation with the acceleration voltage of 50-1000kV to the bottom of reduced pressure of 10<sup>-2</sup> - 10<sup>-7</sup>torr.

[Claim 7] The process of the functional silicon ingredient according to claim 6 which performs electron beam irradiation with the acceleration voltage of 50-1000kV to the bottom of reduced pressure of 10<sup>-3</sup> - 10<sup>-5</sup>torr.

[Claim 8] The process of the functional silicon ingredient according to claim 1 which performs an ion beam exposure using helium ion or Ar ion made to ionize under reduced pressure of 100 - 10<sup>-4</sup>torr to the bottom of the condition of acceleration voltage 100V-10kV and the ion current 0.01 - 100 mA/cm<sup>2</sup>.

[Claim 9] The process of the functional silicon ingredient according to claim 8 which performs an ion beam exposure using helium ion or Ar ion made to ionize under reduced pressure of 10<sup>-1</sup> - 10<sup>-3</sup>torr to the bottom of the condition of acceleration voltage 100V-10kV and the ion current 0.01 - 100 mA/cm<sup>2</sup>.

[Claim 10] The process of the functional silicon ingredient according to claim 8 which performs an ion beam exposure using helium ion or Ar ion made to ionize under reduced pressure of 100 - 10<sup>-4</sup>torr to the bottom of the condition of acceleration voltage 200V-1kV and the ion current 0.1 - 10 mA/cm<sup>2</sup>.

[Claim 11] The process of the functional silicon ingredient according to claim 8 which performs an ion beam exposure using helium ion or Ar ion made to ionize under reduced pressure of 10<sup>-1</sup> - 10<sup>-3</sup>torr to the bottom of the condition of acceleration voltage 100V-10kV and the ion current 0.01 - 100 mA/cm<sup>2</sup>.

[Claim 12] The process of the functional silicon ingredient according to claim 1 which heats under a pressure 760 - 10<sup>-6</sup>torr, and a condition with a temperature of 100-2000 degrees C.

[Claim 13] The process of the functional silicon ingredient according to claim 12 which heats under a pressure 10<sup>-1</sup> - 10<sup>-3</sup>torr, and a 200-1500-degree C condition.

[Claim 14] The process of the functional silicon ingredient according to claim 12 which heats under a 100-2000-degree C condition whenever [ helium / of a pressure 760 - 10<sup>-4</sup>torr /, or Ar ambient atmosphere moderate temperature ].

[Claim 15] The process of the functional silicon ingredient according to claim 14 which heats under a 200-1500-degree C condition whenever [ helium / of a pressure 760 - 10<sup>-4</sup>torr /, or Ar ambient atmosphere moderate temperature ].

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the process of the functional silicon ingredient containing at least one sort of the hollow-onion-like silicon which connotes a silicon nanotube, silicon FURAREN, hollow-onion-like silicon, and a metal.

[0002] in addition, in this invention, the core of "hollow-onion-like silicon" is hollow, and the silicon laminated structure has developed into the onion to the perimeter -- the silicon particle of the shape of spherical or a polyhedron is meant. In such hollow-onion-like silicon, the laminating of the silicon laminating is carried out to dozens of layers from the monolayer.

[0003] moreover, metal particles exist in the hollow of the core of the above-mentioned "hollow-onion-like silicon" with "the hollow-onion-like silicon which connotes a metal" -- the silicon particle of the shape of spherical or a polyhedron is meant. Although especially the metal to connote is not limited, Mg, aluminum, Au, etc. are mentioned, for example.

[0004]

[Description of the Prior Art] Conventionally, the highly efficient carbon material (a carbon nanotube (a "nanotube" may only be told to below), fullerene, hollow-onion-like carbon, hollow-onion-like carbon that connotes a metal) of nano size is compounded by the gaseous phase by the carbon arc process, the spatter, the laser light irradiating method, etc. by using carbon materials, such as amorphism carbon and graphite, as a raw material.

[0005] On the other hand, although there is an example of research of the silicon cluster composition by the gaseous phase about a silicon ingredient, there is no example which compounded the silicon nanotube which replaced the carbon of a functional carbon material with silicon, silicon FURAREN, hollow-onion-like silicon, the hollow-onion-like silicon that connotes a metal. That is, according to the above-mentioned physical approach, a functional carbon material is formed of disassembly of the raw material by high temperature, evaporation, recombination, deposition, etc., but in applying this approach to composition of a silicon system ingredient, there is a trouble that disassembly of a raw material and evaporation cannot take place easily.

[0006] Since the functional silicon ingredient is equipped with the property which was excellent in versatility, if a practical synthetic technique is established, application in large fields, such as an environmental-proof ingredient, a heat-resistant ingredient, an abrasion resistance ingredient, a hydrogen absorption ingredient, an electron ray radiation emitter, and other electronic ingredients, is expected. Furthermore, when the technique which can form the high grade thin film which arranged the functional silicon ingredient on the substrate is established, it is predicted as a thing also with the further increasing usefulness.

[0007]

[Problem(s) to be Solved by the Invention] Therefore, this invention sets it as the main purposes to offer the new technique which compounds functional silicon ingredients, such as a silicon nanotube, silicon FURAREN, hollow-onion-like silicon, and hollow-onion-like silicon that connotes a metal, by high yield and the high grade.

[0008]

[Means for Solving the Problem] this invention person uses as a raw material the polysilane ingredient which has either [ at least ] a reactant double bond or a triple bond, as a result of advancing research in view of the present condition of the above techniques. That the new technique which compounds functional silicon ingredients, such as a silicon nanotube, should be completed, as a result of repeating research wholeheartedly, by using the

electrochemistry reduction-technique The polysilane ingredient (precursor) which has a double bond and/or a triple bond reactant near ordinary temperature is compounded. By irradiating light, an electron ray, an ion beam, etc. at low temperature comparatively at this precursor, or heat-treating this precursor, crosslinking reaction was carried out and it succeeded in manufacturing a functional silicon ingredient.

[0009] That is, this invention offers the new manufacture approach of the functional silicon ingredient shown below.;

1. by irradiating at least one sort of light, an electron ray, and an ion beam to the polysilane ingredient containing at least one sort of  $\text{-Si=Si-}$  and  $\text{-Si}^{**}\text{Si-}$  Or by heating the polysilane ingredient containing at least one sort of  $\text{-Si=Si-}$  and  $\text{-Si}^{**}\text{Si-}$  Or by presenting exposure processing and heat-treatment with the polysilane ingredient containing at least one sort of  $\text{-Si=Si-}$  and  $\text{-Si}^{**}\text{Si-}$  The process of the functional silicon ingredient characterized by making at least one sort of the hollow-onion-like silicon which is made to react and connotes a silicon nanotube, silicon FURAREN, hollow-onion-like silicon, and a metal form.

[0010] 2. Process of functional silicon ingredient given in above-mentioned term 1 using laser light of wavelength of 300-1200nm, output 0.1 - 10 mJ/cm<sup>2</sup> as exposure light.

[0011] 3. Process of functional silicon ingredient given in above-mentioned term 2 using laser light of wavelength of 400-800nm, output 0.5 - 5 mJ/cm<sup>2</sup> as exposure light.

[0012] 4. Process of functional silicon ingredient given in above-mentioned term 1 which performs electron beam irradiation with acceleration voltage of 1-2000kV to the bottom of reduced pressure of 10<sup>-2</sup> - 10<sup>-7</sup>torr.

[0013] 5. Process of functional silicon ingredient given in above-mentioned term 4 which performs electron beam irradiation with acceleration voltage of 1-2000kV to the bottom of reduced pressure of 10<sup>-3</sup> - 10<sup>-5</sup>torr.

[0014] 6. Process of functional silicon ingredient given in above-mentioned term 4 which performs electron beam irradiation with acceleration voltage of 50-1000kV to the bottom of reduced pressure of 10<sup>-2</sup> - 10<sup>-7</sup>torr.

[0015] 7. Process of functional silicon ingredient given in above-mentioned term 6 which performs electron beam irradiation with acceleration voltage of 50-1000kV to the bottom of reduced pressure of 10<sup>-3</sup> - 10<sup>-5</sup>torr.

[0016] 8. Process of functional silicon ingredient given in above-mentioned term 1 which performs ion beam exposure using helium ion or Ar ion made to ionize under reduced pressure of 100 - 10<sup>-4</sup>torr to the bottom of condition of acceleration voltage 100V-10kV and the ion current 0.01 - 100 mA/cm<sup>2</sup>.

[0017] 9. Process of functional silicon ingredient given in above-mentioned term 8 which performs ion beam exposure using helium ion or Ar ion made to ionize under reduced pressure of 10<sup>-1</sup> - 10<sup>-3</sup>torr to the bottom of condition of acceleration voltage 100V-10kV and the ion current 0.01 - 100 mA/cm<sup>2</sup>.

[0018] 10. The process of a functional silicon ingredient given in the above-mentioned term 8 which performs an ion beam exposure using helium ion or Ar ion made to ionize under reduced pressure of 100 - 10<sup>-4</sup>torr to the bottom of the condition of acceleration voltage 200V-1kV and the ion current 0.1 - 10 mA/cm<sup>2</sup>.

[0019] 11. The process of a functional silicon ingredient given in the above-mentioned term 8 which performs an ion beam exposure using helium ion or Ar ion made to ionize under reduced pressure of 10<sup>-1</sup> - 10<sup>-3</sup>torr to the bottom of the condition of acceleration voltage 100V-10kV and the ion current 0.01 - 100 mA/cm<sup>2</sup>.

[0020] 12. The process of a functional silicon ingredient given in the above-mentioned term 1 which heats under a pressure 760 - 10<sup>-6</sup>torr, and a condition with a temperature of 100-2000 degrees C.

[0021] 13. The process of a functional silicon ingredient given in the above-mentioned term 12 which heats under a pressure 10<sup>-1</sup> - 10<sup>-3</sup>torr, and a 200-1500-degree C condition.

[0022] 14. The process of a functional silicon ingredient given in the above-mentioned term 12 which heats under a 100-2000-degree C condition whenever [ helium / of a pressure 760 - 10<sup>-4</sup>torr /, or Ar ambient atmosphere moderate temperature ].

[0023] 15. The process of a functional silicon ingredient given in the above-mentioned term 14 which heats under

a 200-1500-degree C condition whenever [ helium / of a pressure 760 - 10<sup>-4</sup>torr / , or Ar ambient atmosphere moderate temperature ].

[0024]

[Embodiment of the Invention] As compared with the conventional approach, this invention approach is a half-chemical synthesis method under mild conditions, and is the technique of manufacturing the new functional silicon ingredient which assembles structure by the chemical reaction and goes.

[0025] All or some of side chain carries out dehalogenation of the polysilane permuted with the halogen by electrode reduction, and the polysilane ingredient which has at least one sort of the reactant double bond which serves as a raw material in this invention approach, and a triple bond compounds the polysilane ingredient which has a double bond and/or a triple bond.

[0026] The polysilane by which all or some of side chain is permuted with the halogen is a well-known ingredient, for example, the process is reported to JP,63-233007,A etc. in detail. Therefore, the process is not limited, and can also mix and use two or more sorts which are [ molecular weight / a permutation condition, ] different. In the polysilane derivative by which some side chains are permuted with the halogen, any side chain radicals other than a halogen are not limited to these, although hydrogen, methyl, phenyl, etc. are illustrated.

[0027] Moreover, in order for the above-mentioned side chain to compound the polysilane ingredient which has a double bond and/or a triple bond from the polysilane permuted with the halogen, electrode electrolytic reduction is performed. It is desirable to use reactant electrodes, such as Mg, aluminum, and Zn, as a working electrode in three electrode methods as an anode plate in the nonaqueous solvent which dissolved the supporting electrolyte and the energization assistant on the occasion of electrolytic reduction in two electrode methods.

[0028] On the occasion of electrolytic reduction, one sort or these alloys of magnesium, aluminum, and zinc are used as a reactant electrode (namely, the anode plate in two electrode methods or the counter-electrode in three electrode methods). Especially as these alloys, although not limited, a magnesia alloy ("magnox";Mg=98.89%, aluminum=1%, calcium=0.1%, Ba=0.01%), an aluminium alloy ("duralumin";aluminum=95%, Cu=4.6%, Mg=0.5%), a zinc-aluminium alloy (Zn=78%, aluminum=22%), etc. are illustrated.

[0029] Moreover, the ingredient of the cathode in two electrode methods and the working electrode in three electrode methods, especially a configuration, etc. are not limited. Stainless steel, carbon, platinum, gold, etc. are illustrated as these ingredients. An electrode configuration can choose the configuration of arbitration, such as a wire, a mesh, and a plate.

[0030] As a supporting electrolyte, LiCl, LiClO<sub>4</sub> and LiBF<sub>4</sub>, NH<sub>4</sub>Cl, NH<sub>4</sub>ClO<sub>4</sub>, NH<sub>4</sub>BF<sub>4</sub>, 4(CH<sub>3</sub>) NCl, 4(CH<sub>3</sub>) NClO<sub>4</sub>, 4(CH<sub>3</sub>) NBF<sub>4</sub>, etc. are mentioned. In these, LiCl is more desirable. The operating rate of a supporting electrolyte is usually about 0.01 - 10 % of the weight to a solvent, and is about 0.5 - 5 % of the weight more preferably.

[0031] As an energization assistant, FeCl<sub>2</sub>, Fe (ClO<sub>4</sub>)<sub>2</sub>, Fe (BF<sub>4</sub>)<sub>2</sub>, etc. are mentioned, and FeCl<sub>2</sub> is more desirable in these. The operating rate of an energization assistant is usually about 0.1 - 30 % of the weight to a solvent, and is about 1 - 20 % of the weight more preferably.

[0032] As a nonaqueous solvent, a tetrahydrofuran, N,N-dimethylformamide, an acetonitrile, etc. are mentioned and a tetrahydrofuran is more desirable in these. The amount of the nonaqueous solvent used is usually about 20-200 weight twice to the aromatic hydrocarbon derivative which has a halogen atom, and is about 50-100 weight twice preferably.

[0033] In an electrolytic reduction reaction, when an electron moves to the polysilane derivative which has the halogen atom which is a reaction raw material and the functional group desorbed from the reaction intermediate \*\*\*\*s as an anion, a silicon radical generates to a polysilane derivative and an adjacent silicon radical carries out coupling to it. When this reaction advances continuously, the silicon ingredient with which the multiple bond

developed into altitude is obtained from a polysilane derivative. However, in this electrolytic reduction reaction, an adjacent silicon radical is accompanied also by side reaction, such as decomposition in coupling (crosslink) of the silicon radical which it not only carries out coupling, but exists in a different molecule, and the generic point of a silicon radical, and disproportionation.

[0034] in order [ then, ] to reduce side reaction --  $M(dppe)_2X_2$  -- among a formula, Fe, Co, or nickel; X adds Cl, Br, or I] as a catalyst, and M gives priority to a main reaction. This operating rate of  $M(dppe)_2X_2$  is usually about 0.01 - 5 % of the weight to a solvent, and is about 0.1 - 2 % of the weight more preferably.

[0035] As for the electrode electrolytic reduction of this invention, it is desirable to carry out under inert gas, such as nitrogen, argon gas, and helium.

[0036] On the occasion of the electrode electrolytic reduction of this invention, an about [ 5-50V ] electrical potential difference is usually impressed, and an about [ 10-30V ] electrical potential difference is impressed more preferably.

[0037] Moreover, the temperature at the time of the electrode electrolytic reduction of this invention is usually within the limits of about -20-10 degrees C, and is within the limits of about -10-5 degrees C more preferably. Reaction time is usually within the limits of about 5 - 24 hours, and is within the limits of about 8 - 12 hours more preferably.

[0038] The silicon ingredient obtained by this invention approach includes either [ at least ] a double bond (-Si=Si-) or a triple bond (-Si\*\*Si-).

[0039] The attempt which compounds functional silicon ingredients, such as a silicon nanotube, by using a polysilane ingredient including such a reactant double bond and/or a reactant triple bond as a raw material is not made conventionally.

[0040] By carrying out exposure processing of at least one sort of light (for example, laser light), an electron ray, and an ion beam to this in this invention by making a polysilane ingredient including a reactant double bond and/or a reactant triple bond into a precursor By heat-treating such a polysilane ingredient, or or by exposure-processing and heat-treating such a polysilane ingredient The ingredient or thin film which consists of a silicon nanotube, silicon FURAREN, hollow-onion-like silicon, hollow-onion-like silicon that connotes a metal, or two or more sorts of such inclusion (it may be called the "purpose product" below) is obtained.

[0041] Composition of the purpose product can be performed by irradiating at least one sort, such as light, such as laser light, an electron beam, and an ion beam, or heat-treating a raw material polysilane ingredient to the above-mentioned raw material polysilane ingredient, or exposure-processing, and heat-treating a raw material polysilane ingredient (the sequence of both processings not being asked), and producing a reaction within a raw material.

[0042] In performing an optical exposure to a raw material polysilane ingredient, it usually uses the wavelength of about 400-800nm, an output 0.5 - about two 5 mJ/cm laser light more preferably the wavelength of about 300-1200nm, an output 0.1 - about two 10 mJ/cm. Although what is usually used can be used for the class of laser light and it is not restricted especially, Nd:YAG laser, Ti:Sa laser, Dye laser, Dye+SHG laser, Ar+ laser, Kr+ laser, etc. are mentioned, for example.

[0043] In performing electron beam irradiation to a raw material polysilane ingredient, it usually irradiates the bottom of reduced pressure of  $10^{-2}$  -  $10^{-7}$  torr extent (preferably  $10^{-3}$  -  $10^{-5}$  torr extent) with the acceleration voltage of about (preferably about 50-1000kV) 1-2000kV.

[0044] In performing an ion beam exposure, it arranges a raw material polysilane ingredient in a reduced pressure chamber (they are usually  $10^{-1}$  -  $10^{-3}$  torr extent more preferably than  $10^0$  -  $10^{-4}$  torr extent;). The bottom of an about (preferably 200 about V-1kV) acceleration voltage 100V-10kV and the ion current 0.01 - about (preferably about two 0.1 - 10 mA/cm) two 100 mA/cm condition is irradiated using helium ion or Ar ion made to ionize.

[0045] When irradiating in order to give reaction energy to a raw material polysilane ingredient, it is more desirable as a source of an exposure to use laser light.

[0046] In heating a raw material polysilane ingredient, it usually heats at about (preferably about 200-1500 degrees C) 100-2000 degrees C under reduced pressure of 760 - 10-6torr extent (preferably 10 under the pressure of -1 - 10-3torr extent). Or a polysilane ingredient may be heated at about (preferably about 200-1500 degrees C) 100-2000 degrees C among helium of 760 - 10-4torr extent, or Ar ambient atmosphere.

[0047] Furthermore, on the occasion of processing of a raw material polysilane ingredient, at least one sort and heat-treatment of the above-mentioned exposure processing may be used together.

[0048]

[Effect of the Invention] According to this invention, the following remarkable effectiveness is attained.

[0049] (1) A silicon nanotube, silicon FURAREN, hollow-onion-like silicon, and metal-endocyst-onion-like silicon are producible by irradiating at least one sort of light, an electron beam, and an ion beam, or heat-treating such a polysilane ingredient to the polysilane ingredient containing either [ at least ] -Si=Si- or -Si\*\*Si-, or exposure-processing and heat-treating such a polysilane ingredient.

[0050] (2) choosing suitably the exposure processing and heat-treatment by light, the electron beam, and the ion beam as a processing means of a polysilane ingredient -- or either a silicon nanotube, silicon FURAREN, hollow-onion-like silicon and metal-endocyst-onion-like silicon are alternatively producible by combining two or more processings.

[0051] (3) Therefore, the functional silicon ingredient by this invention is useful as an environmental-proof ingredient, a heat-resistant ingredient, an abrasion resistance ingredient, a hydrogen absorption ingredient, an electron ray radiation emitter, other electronic ingredients, etc.

[0052]

[Example] It compounded by the approach of showing an example 1 functionality silicon ingredient below.

[0053] Polysilane (HO-(Si (CH<sub>3</sub>) (C<sub>6</sub>H<sub>5</sub>)) n-OH:n=50) is used as a raw material. Polysilane is chlorinated and it is a chlorination object (HO- (after forming n-OH) (Si (CH<sub>3</sub>) (C<sub>6</sub>H<sub>5</sub>)) (Si (CH<sub>3</sub>) (Cl))). According to the approach of carrying out electrolytic reduction of the polytetrafluoroethylene film shown in JP,8-335702,A in a reactant anode plate, the polysilane ingredient with the part which has a double bond was compounded.

[0054] That is, with the following solvents, the chlorination object of the above-mentioned polysilane was prepared into the flask, and was dissolved. <BR> [0055]

Tetrahydrofuran 30ml lithium chloride 0.8g ferrous chloride The vacuum drying was carried out, after having impressed the electrical potential difference of 40V between the anode plate (magnesium) installed in the flask, and cathode (stainless steel), having returned at 0 degree C for 10 hours, obtaining the polysilane powder which the double bond generated and washing this by the tetrahydrofuran subsequently to argon gas 0.48g, carrying out bubbling by argon gas after permuting the inside of a flask. The polysilane thin film was made to form on a substrate with a spin coat method by using the obtained product as a toluene solution 25%.

[0056] After carrying out embedding of the polysilane thin film including the prepared double bond to the epoxy resin and cutting using a microtome for the electron-beam-irradiation processing by the transmission electron microscope (TEM:HITACHI H7100), the sample electrode holder was heated at 800 degrees C under the high vacuum of 10-6torr, and the electron ray was irradiated with the acceleration voltage of 100kV.

[0057] Consequently, it has been checked with the transmission electron microscope that the silicon nanotube had been formed into the sample.

[0058] After carrying out embedding of the polysilane ingredient sample including the double bond produced like example 2 example 1 to the epoxy resin and cutting using a microtome for the electron-beam-irradiation processing by the transmission electron microscope (TEM:HITACHI H7100), the sample electrode holder was

heated at 300 degrees C under the high vacuum of 10-6torr, and the electron ray was irradiated with the acceleration voltage of 100kV.

[0059] Consequently, it has been checked with the transmission electron microscope that the onion-like silicon which connotes a magnesium particle had been formed into the sample. In case this magnesium particle returns a raw material, it is considered that the magnesium ion generated from the anode plate deposited in the thin film as metal magnesium.

[0060] The onion-like silicon sample which connotes the magnesium particle produced like example 3 example 2 was raised to actuation of an example 2, sample electrode-holder temperature was succeedingly raised to 800 degrees C, and it held for 10 minutes. Consequently, the magnesium particle by which endocyst was carried out carried out melting evaporation, and was removed, and hollow-onion-like silicon was formed into the sample.

[0061] The ion beam (Kauffmann mold ion source: an argon ion beam, acceleration voltage:500V, ion current consistency:1mA/cm<sup>2</sup>) was irradiated for 10 minutes in the reduced pressure chamber (4x10<sup>-2</sup>torr) to the polysilane ingredient sample including the double bond produced like example 4 example 1.

[0062] After extracting and condensing this sample with toluene, it dissociated by HPLC (column: KOSUMO seal Buckyrep pack DOKARAMU). By 13 C-NMR, it has checked that silicon FURAREN was formed.

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[Translation done.]

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**TECHNICAL FIELD**

[Field of the Invention] This invention relates to the process of the functional silicon ingredient containing at least one sort of the hollow-onion-like silicon which connotes a silicon nanotube, silicon FURAREN, hollow-onion-like silicon, and a metal.

[0002] in addition, in this invention, the core of "hollow-onion-like silicon" is hollow, and the silicon laminated structure has developed into the onion to the perimeter -- the silicon particle of the shape of spherical or a polyhedron is meant. In such hollow-onion-like silicon, the laminating of the silicon laminating is carried out to dozens of layers from the monolayer.

[0003] moreover, metal particles exist in the hollow of the core of the above-mentioned "hollow-onion-like silicon" with "the hollow-onion-like silicon which connotes a metal" -- the silicon particle of the shape of spherical or a polyhedron is meant. Although especially the metal to connote is not limited, Mg, aluminum, Au, etc. are mentioned, for example.

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**PRIOR ART**

[Description of the Prior Art] Conventionally, the highly efficient carbon material (a carbon nanotube (a "nanotube" may only be told to below), fullerene, hollow-onion-like carbon, hollow-onion-like carbon that connotes a metal) of nano size is compounded by the gaseous phase by the carbon arc process, the spatter, the laser light irradiating method, etc. by using carbon materials, such as amorphous carbon and graphite, as a raw material.

[0005] On the other hand, although there is an example of research of the silicon cluster composition by the gaseous phase about a silicon ingredient, there is no example which compounded the silicon nanotube which replaced the carbon of a functional carbon material with silicon, silicon FURAREN, hollow-onion-like silicon, the hollow-onion-like silicon that connotes a metal. That is, according to the above-mentioned physical approach, a functional carbon material is formed of disassembly of the raw material by high temperature, evaporation, recombination, deposition, etc., but in applying this approach to composition of a silicon system ingredient, there is a trouble that disassembly of a raw material and evaporation cannot take place easily.

[0006] Since the functional silicon ingredient is equipped with the property which was excellent in versatility, if a practical synthetic technique is established, application in large fields, such as an environmental-proof ingredient, a heat-resistant ingredient, an abrasion resistance ingredient, a hydrogen absorption ingredient, an electron ray radiation emitter, and other electronic ingredients, is expected. Furthermore, when the technique which can form the high grade thin film which arranged the functional silicon ingredient on the substrate is established, it is predicted as a thing also with the further increasing usefulness.

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**EFFECT OF THE INVENTION**

[Effect of the Invention] According to this invention, the following remarkable effectiveness is attained.

[0049] (1) A silicon nanotube, silicon FURAREN, hollow-onion-like silicon, and metal-endocyst-onion-like silicon are producible by irradiating at least one sort of light, an electron beam, and an ion beam, or heat-treating



such a polysilane ingredient to the polysilane ingredient containing either [ at least ] -Si=Si- or -Si\*\*Si-, or exposure-processing and heat-treating such a polysilane ingredient.

[0050] (2) choosing suitably the exposure processing and heat-treatment by light, the electron beam, and the ion beam as a processing means of a polysilane ingredient -- or either a silicon nanotube, silicon FURAREN, hollow-onion-like silicon and metal-endocyst-onion-like silicon are alternatively producible by combining two or more processings.

[0051] (3) Therefore, the functional silicon ingredient by this invention is useful as an environmental-proof ingredient, a heat-resistant ingredient, an abrasion resistance ingredient, a hydrogen absorption ingredient, an electron ray radiation emitter, other electronic ingredients, etc.

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**TECHNICAL PROBLEM**

[Problem(s) to be Solved by the Invention] Therefore, this invention sets it as the main purposes to offer the new technique which compounds functional silicon ingredients, such as a silicon nanotube, silicon FURAREN, hollow-onion-like silicon, and hollow-onion-like silicon that connotes a metal, by high yield and the high grade.

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**MEANS**

[Means for Solving the Problem] this invention person uses as a raw material the polysilane ingredient which has either [ at least ] a reactant double bond or a triple bond, as a result of advancing research in view of the present condition of the above techniques. That the new technique which compounds functional silicon ingredients, such as a silicon nanotube, should be completed, as a result of repeating research wholeheartedly, by using the electrochemistry reduction-technique The polysilane ingredient (precursor) which has a double bond and/or a

triple bond reactant near ordinary temperature is compounded. By irradiating light, an electron ray, an ion beam, etc. at low temperature comparatively at this precursor, or heat-treating this precursor, crosslinking reaction was carried out and it succeeded in manufacturing a functional silicon ingredient.

[0009] That is, this invention offers the new manufacture approach of the functional silicon ingredient shown below.;

1. by irradiating at least one sort of light, an electron ray, and an ion beam to the polysilane ingredient containing at least one sort of -Si=Si- and -Si\*\*Si- Or by heating the polysilane ingredient containing at least one sort of -Si=Si- and -Si\*\*Si- Or by presenting exposure processing and heat-treatment with the polysilane ingredient containing at least one sort of -Si=Si- and -Si\*\*Si- The process of the functional silicon ingredient characterized by making at least one sort of the hollow-onion-like silicon which is made to react and connotes a silicon nanotube, silicon FURAREN, hollow-onion-like silicon, and a metal form.

[0010] 2. Process of functional silicon ingredient given in above-mentioned term 1 using laser light of wavelength of 300-1200nm, output 0.1 - 10 mJ/cm<sup>2</sup> as exposure light.

[0011] 3. Process of functional silicon ingredient given in above-mentioned term 2 using laser light of wavelength of 400-800nm, output 0.5 - 5 mJ/cm<sup>2</sup> as exposure light.

[0012] 4. Process of functional silicon ingredient given in above-mentioned term 1 which performs electron beam irradiation with acceleration voltage of 1-2000kV to the bottom of reduced pressure of 10<sup>-2</sup> - 10<sup>-7</sup>torr.

[0013] 5. Process of functional silicon ingredient given in above-mentioned term 4 which performs electron beam irradiation with acceleration voltage of 1-2000kV to the bottom of reduced pressure of 10<sup>-3</sup> - 10<sup>-5</sup>torr.

[0014] 6. Process of functional silicon ingredient given in above-mentioned term 4 which performs electron beam irradiation with acceleration voltage of 50-1000kV to the bottom of reduced pressure of 10<sup>-2</sup> - 10<sup>-7</sup>torr.

[0015] 7. Process of functional silicon ingredient given in above-mentioned term 6 which performs electron beam irradiation with acceleration voltage of 50-1000kV to the bottom of reduced pressure of 10<sup>-3</sup> - 10<sup>-5</sup>torr.

[0016] 8. Process of functional silicon ingredient given in above-mentioned term 1 which performs ion beam exposure using helium ion or Ar ion made to ionize under reduced pressure of 100 - 10<sup>-4</sup>torr to the bottom of condition of acceleration voltage 100V-10kV and the ion current 0.01 - 100 mA/cm<sup>2</sup>.

[0017] 9. Process of functional silicon ingredient given in above-mentioned term 8 which performs ion beam exposure using helium ion or Ar ion made to ionize under reduced pressure of 10<sup>-1</sup> - 10<sup>-3</sup>torr to the bottom of condition of acceleration voltage 100V-10kV and the ion current 0.01 - 100 mA/cm<sup>2</sup>.

[0018] 10. The process of a functional silicon ingredient given in the above-mentioned term 8 which performs an ion beam exposure using helium ion or Ar ion made to ionize under reduced pressure of 100 - 10<sup>-4</sup>torr to the bottom of the condition of acceleration voltage 200V-1kV and the ion current 0.1 - 10 mA/cm<sup>2</sup>.

[0019] 11. The process of a functional silicon ingredient given in the above-mentioned term 8 which performs an ion beam exposure using helium ion or Ar ion made to ionize under reduced pressure of 10<sup>-1</sup> - 10<sup>-3</sup>torr to the bottom of the condition of acceleration voltage 100V-10kV and the ion current 0.01 - 100 mA/cm<sup>2</sup>.

[0020] 12. The process of a functional silicon ingredient given in the above-mentioned term 1 which heats under a pressure 760 - 10<sup>-6</sup>torr, and a condition with a temperature of 100-2000 degrees C.

[0021] 13. The process of a functional silicon ingredient given in the above-mentioned term 12 which heats under a pressure 10<sup>-1</sup> - 10<sup>-3</sup>torr, and a 200-1500-degree C condition.

[0022] 14. The process of a functional silicon ingredient given in the above-mentioned term 12 which heats under a 100-2000-degree C condition whenever [ helium / of a pressure 760 - 10<sup>-4</sup>torr /, or Ar ambient atmosphere moderate temperature ].

[0023] 15. The process of a functional silicon ingredient given in the above-mentioned term 14 which heats under a 200-1500-degree C condition whenever [ helium / of a pressure 760 - 10<sup>-4</sup>torr /, or Ar ambient atmosphere

moderate temperature ].

[0024]

[Embodiment of the Invention] As compared with the conventional approach, this invention approach is a half-chemical synthesis method under mild conditions, and is the technique of manufacturing the new functional silicon ingredient which assembles structure by the chemical reaction and goes.

[0025] All or some of side chain carries out dehalogenation of the polysilane permuted with the halogen by electrode reduction, and the polysilane ingredient which has at least one sort of the reactant double bond which serves as a raw material in this invention approach, and a triple bond compounds the polysilane ingredient which has a double bond and/or a triple bond.

[0026] The polysilane by which all or some of side chain is permuted with the halogen is a well-known ingredient, for example, the process is reported to JP,63-233007,A etc. in detail. Therefore, the process is not limited, and can also mix and use two or more sorts which are [ molecular weight / a permutation condition, ] different. In the polysilane derivative by which some side chains are permuted with the halogen, any side chain radicals other than a halogen are not limited to these, although hydrogen, methyl, phenyl, etc. are illustrated.

[0027] Moreover, in order for the above-mentioned side chain to compound the polysilane ingredient which has a double bond and/or a triple bond from the polysilane permuted with the halogen, electrode electrolytic reduction is performed. It is desirable to use reactant electrodes, such as Mg, aluminum, and Zn, as a working electrode in three electrode methods as an anode plate in the nonaqueous solvent which dissolved the supporting electrolyte and the energization assistant on the occasion of electrolytic reduction in two electrode methods.

[0028] On the occasion of electrolytic reduction, one sort or these alloys of magnesium, aluminum, and zinc are used as a reactant electrode (namely, the anode plate in two electrode methods or the counter-electrode in three electrode methods). Especially as these alloys, although not limited, a magnesia alloy ("magnox";Mg=98.89%, aluminum=1%, calcium=0.1%, Ba=0.01%), an aluminium alloy ("duralumin";aluminum=95%, Cu=4.6%, Mg=0.5%), a zinc-aluminium alloy (Zn=78%, aluminum=22%), etc. are illustrated.

[0029] Moreover, the ingredient of the cathode in two electrode methods and the working electrode in three electrode methods, especially a configuration, etc. are not limited. Stainless steel, carbon, platinum, gold, etc. are illustrated as these ingredients. An electrode configuration can choose the configuration of arbitration, such as a wire, a mesh, and a plate.

[0030] As a supporting electrolyte, LiCl, LiClO<sub>4</sub> and LiBF<sub>4</sub>, NH<sub>4</sub>Cl, NH<sub>4</sub>ClO<sub>4</sub>, NH<sub>4</sub>BF<sub>4</sub>, 4(CH<sub>3</sub>) NCl, 4(CH<sub>3</sub>) NClO<sub>4</sub>, 4(CH<sub>3</sub>) NBF<sub>4</sub>, etc. are mentioned. In these, LiCl is more desirable. The operating rate of a supporting electrolyte is usually about 0.01 - 10 % of the weight to a solvent, and is about 0.5 - 5 % of the weight more preferably.

[0031] As an energization assistant, FeCl<sub>2</sub>, Fe (ClO<sub>4</sub>)<sub>2</sub>, Fe (BF<sub>4</sub>)<sub>2</sub>, etc. are mentioned, and FeCl<sub>2</sub> is more desirable in these. The operating rate of an energization assistant is usually about 0.1 - 30 % of the weight to a solvent, and is about 1 - 20 % of the weight more preferably.

[0032] As a nonaqueous solvent, a tetrahydrofuran, N,N-dimethylformamide, an acetonitrile, etc. are mentioned and a tetrahydrofuran is more desirable in these. The amount of the nonaqueous solvent used is usually about 20-200 weight twice to the aromatic hydrocarbon derivative which has a halogen atom, and is about 50-100 weight twice preferably.

[0033] In an electrolytic reduction reaction, when an electron moves to the polysilane derivative which has the halogen atom which is a reaction raw material and the functional group desorbed from the reaction intermediate \*\*\*\*s as an anion, a silicon radical generates to a polysilane derivative and an adjacent silicon radical carries out coupling to it. When this reaction advances continuously, the silicon ingredient with which the multiple bond developed into altitude is obtained from a polysilane derivative. However, in this electrolytic reduction reaction,

an adjacent silicon radical is accompanied also by side reaction, such as decomposition in coupling (crosslink) of the silicon radical which it not only carries out coupling, but exists in a different molecule, and the generic point of a silicon radical, and disproportionation.

[0034] in order [ then, ] to reduce side reaction --  $M(dppe)_2X_2$  -- among a formula, Fe, Co, or nickel; X adds Cl, Br, or I as a catalyst, and M gives priority to a main reaction. This operating rate of  $M(dppe)_2X_2$  is usually about 0.01 - 5 % of the weight to a solvent, and is about 0.1 - 2 % of the weight more preferably.

[0035] As for the electrode electrolytic reduction of this invention, it is desirable to carry out under inert gas, such as nitrogen, argon gas, and helium.

[0036] On the occasion of the electrode electrolytic reduction of this invention, an about [ 5-50V ] electrical potential difference is usually impressed, and an about [ 10-30V ] electrical potential difference is impressed more preferably.

[0037] Moreover, the temperature at the time of the electrode electrolytic reduction of this invention is usually within the limits of about -20-10 degrees C, and is within the limits of about -10-5 degrees C more preferably. Reaction time is usually within the limits of about 5 - 24 hours, and is within the limits of about 8 - 12 hours more preferably.

[0038] The silicon ingredient obtained by this invention approach includes either [ at least ] a double bond (-Si=Si-) or a triple bond (-Si\*\*Si-).

[0039] The attempt which compounds functional silicon ingredients, such as a silicon nanotube, by using a polysilane ingredient including such a reactant double bond and/or a reactant triple bond as a raw material is not made conventionally.

[0040] By carrying out exposure processing of at least one sort of light (for example, laser light), an electron ray, and an ion beam to this in this invention by making a polysilane ingredient including a reactant double bond and/or a reactant triple bond into a precursor By heat-treating such a polysilane ingredient, or or by exposure-processing and heat-treating such a polysilane ingredient The ingredient or thin film which consists of a silicon nanotube, silicon FURAREN, hollow-onion-like silicon, hollow-onion-like silicon that connotes a metal, or two or more sorts of such inclusion (it may be called the "purpose product" below) is obtained.

[0041] Composition of the purpose product can be performed by irradiating at least one sort, such as light, such as laser light, an electron beam, and an ion beam, or heat-treating a raw material polysilane ingredient to the above-mentioned raw material polysilane ingredient, or exposure-processing, and heat-treating a raw material polysilane ingredient (the sequence of both processings not being asked), and producing a reaction within a raw material.

[0042] In performing an optical exposure to a raw material polysilane ingredient, it usually uses the wavelength of about 400-800nm, an output 0.5 - about two 5 mJ/cm laser light more preferably the wavelength of about 300-1200nm, an output 0.1 - about two 10 mJ/cm. Although what is usually used can be used for the class of laser light and it is not restricted especially, Nd:YAG laser, Ti:Sa laser, Dye laser, Dye+SHG laser, Ar+ laser, Kr+ laser, etc. are mentioned, for example.

[0043] In performing electron beam irradiation to a raw material polysilane ingredient, it usually irradiates the bottom of reduced pressure of  $10^{-2}$  -  $10^{-7}$  torr extent (preferably  $10^{-3}$  -  $10^{-5}$  torr extent) with the acceleration voltage of about (preferably about 50-1000kV) 1-2000kV.

[0044] In performing an ion beam exposure, it arranges a raw material polysilane ingredient in a reduced pressure chamber (they are usually  $10^{-1}$  -  $10^{-3}$  torr extent more preferably than  $10^{-2}$  -  $10^{-4}$  torr extent). The bottom of an about (preferably 200 about V-1kV) acceleration voltage 100V-10kV and the ion current 0.01 - about (preferably about two 0.1 - 10 mA/cm) two 100 mA/cm condition is irradiated using helium ion or Ar ion made to ionize.

[0045] When irradiating in order to give reaction energy to a raw material polysilane ingredient, it is more

desirable as a source of an exposure to use laser light.

[0046] In heating a raw material polysilane ingredient, it usually heats at about (preferably about 200-1500 degrees C) 100-2000 degrees C under reduced pressure of 760 - 10-6torr extent (preferably 10 under the pressure of -1 - 10-3torr extent). Or a polysilane ingredient may be heated at about (preferably about 200-1500 degrees C) 100-2000 degrees C among helium of 760 - 10-4torr extent, or Ar ambient atmosphere.

[0047] Furthermore, on the occasion of processing of a raw material polysilane ingredient, at least one sort and heat-treatment of the above-mentioned exposure processing may be used together.

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[Translation done.]

**\* NOTICES \***

**JP0 and NCIP1 are not responsible for any damages caused by the use of this translation.**

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

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**EXAMPLE**

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[Example] It compounded by the approach of showing an example 1 functionality silicon ingredient below.

[0053] Polysilane (HO-(Si (CH<sub>3</sub>) (C<sub>6</sub>H<sub>5</sub>)) n-OH:n=50) is used as a raw material. Polysilane is chlorinated and it is a chlorination object (HO- (after forming n-OH) (Si (CH<sub>3</sub>) (C<sub>6</sub>H<sub>5</sub>)) (Si (CH<sub>3</sub>) (Cl))). According to the approach of carrying out electrolytic reduction of the polytetrafluoroethylene film shown in JP,8-335702,A in a reactant anode plate, the polysilane ingredient with the part which has a double bond was compounded.

[0054] That is, with the following solvents, the chlorination object of the above-mentioned polysilane was prepared into the flask, and was dissolved.

[0055]

Tetrahydrofuran 30ml lithium chloride 0.8g ferrous chloride The vacuum drying was carried out, after having impressed the electrical potential difference of 40V between the anode plate (magnesium) installed in the flask, and cathode (stainless steel), having returned at 0 degree C for 10 hours, obtaining the polysilane powder which the double bond generated and washing this by the tetrahydrofuran subsequently to argon gas 0.48g, carrying out bubbling by argon gas after permuting the inside of a flask. The polysilane thin film was made to form on a substrate with a spin coat method by using the obtained product as a toluene solution 25%.

[0056] After carrying out embedding of the polysilane thin film including the prepared double bond to the epoxy resin and cutting using a microtome for the electron-beam-irradiation processing by the transmission electron microscope (TEM:HITACHI H7100), the sample electrode holder was heated at 800 degrees C under the high vacuum of 10-6torr, and the electron ray was irradiated with the acceleration voltage of 100kV.

[0057] Consequently, it has been checked with the transmission electron microscope that the silicon nanotube had been formed into the sample.

[0058] After carrying out embedding of the polysilane ingredient sample including the double bond produced like example 2 example 1 to the epoxy resin and cutting using a microtome for the electron-beam-irradiation processing by the transmission electron microscope (TEM:HITACHI H7100), the sample electrode holder was heated at 300 degrees C under the high vacuum of 10-6torr, and the electron ray was irradiated with the

acceleration voltage of 100kV.

[0059] Consequently, it has been checked with the transmission electron microscope that the onion-like silicon which connotes a magnesium particle had been formed into the sample. In case this magnesium particle returns a raw material, it is considered that the magnesium ion generated from the anode plate deposited in the thin film as metal magnesium.

[0060] The onion-like silicon sample which connotes the magnesium particle produced like example 3 example 2 was raised to actuation of an example 2, sample electrode-holder temperature was succeedingly raised to 800 degrees C, and it held for 10 minutes. Consequently, the magnesium particle by which endocyst was carried out carried out melting evaporation, and was removed, and hollow-onion-like silicon was formed into the sample.

[0061] The ion beam (Kauffmann mold ion source: an argon ion beam, acceleration voltage:500V, ion current consistency:1mA/cm<sup>2</sup>) was irradiated for 10 minutes in the reduced pressure chamber (4x10<sup>-2</sup>torr) to the polysilane ingredient sample including the double bond produced like example 4 example 1.

[0062] After extracting and condensing this sample with toluene, it dissociated by HPLC (column: KOSUMO seal Buckyprep pack DOKARAMU). By 13 C-NMR, it has checked that silicon FURAREN was formed.

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[Translation done.]